FLUOROVINYL ETHERS AND POLYMERS OBTAINABLE THEREFROM

The present invention relates to Fluorovinyl ethers, the process for preparing them and the polymers obtainable therefrom.

It is well known that perfluoroalkyl vinyl ethers are generally used as monomers for the olefin copolymerization, specifically copolymerization with tetrafluoroethylene, vinylidene fluoride, chlorotrifluoroethylene (CTFE),and/or hexafluoropropene. The introduction of small amounts of perfluoroalkyl vinyl ethers in plastomeric polymers implies a higher polymer processability and better hot mechanical properties. The introduction of high amounts of perfluorovinyl ethers in crosslinkable fluoropolymers implies elastomeric oroperties at low temperature of fluorinated rubbers.

The need was felt, in the fluorinated polymeric material field, to produce both plastomers having good properties at high temperatures, and elastomers having improved properties at low temperatures by using only one fluorovinyl ether.

Such properties at low temperatures can generally be expressed by the glass transition temperature Tg.

Furthermore the need was felt to have available amorphous or crystalline copolymers having a low content of C(O)F end groups. A lower content of C(O)F end groups leads to obtain polymers having a higher thermal stability. A lower Tg allows to have elastomeric polymers which can be used at lower temperatures and therefore to have available elastomers with a wider use range. To obtain the combination of the above mentioned properties, fluorovinyl ethers must have a high

unitary capability to modify the base backbone properties, as well as high reactivity to be used as comonomers both in plastomeric and in elastomeric fluoropolymers. It was desirable to have available vinyl ethers obtainable by simple processes having a limited number of steps. Preferably it would be desirable to have available a continuous process for preparing said vinyl ethers.

To solve the above identicated technical problem, fluorovinyl ethers having different structural properties, have been proposed in the prior art. However from the prior art, hereinafter described, various unsolved problems result evident in the perfluorovinyl ether synthesis and in the preparation of the correspondig polymers having the combination of the above mentioned properties.

Patent USP 3,132,123 describes the preparation of perfluoroalkyl vinyl ethers, of the corresponding homopolymers and copolymers with TFE. Homopolymers are obtained under extreme experimental conditions, by using polymerization pressures from 4,000 to 18,000 atm. The perfluoromethylvinylether (PMVE) homopolymer is an elastomer: the Tg is not reported.

The general formula of the described vinyl ethers is the following:

$$CF_2=CFOR^0_F$$
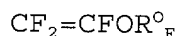
wherein R^0_F is a perfluoroalkyl radical preferably from 1 to 5 carbon atoms. A process for preparing these vinyl ethers is described in Patent USP 3,291,843 wherein the starting acylfluoride is salified and pyrolized with carbonates also in the presence of solvents. By this process undesired hydrogenated by products are obtained.

Patent USP 3,450,684 relates to vinyl ethers having the formula:

$$CF_2=CFO(CF_2CFX^0O)_n, CF_2CF_2X^0$$
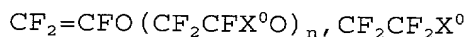
wherein X^0 = F, Cl, CF_3, H and n' can range from 1 to 20. Also

homopolymers obtained by UV polymerization are reported. The exemplified copolymers are not characterized by their properties at low temperatures.

Patent USP 3,635,926 relates to the emulsion copolymerization of perfluorovinyl ethers with TFE, showing that the presence of -C(O)F acylfluoride end groups makes the polymers unstable. The same phenomenon was already reported in USP 3,085,083 in the perfluorovinyl ether polymerization systems in solvent.

Patent USP 3,817,960 relates to the preparation and polymerization of perfluorovinyl ethers having the formula

$$CF_3O(CF_2O)_{n''}CF_2CF_2OCF=CF_2$$

wherein n'' can range from 1 to 5. The compound synthesis is complex, it requires three steps. The preparation of the starting compound $CF_3O(CF_2O)_{n''}CF_2C(O)F$ is carried out by oxidation at low temperature in the presence of U.V. radiations; besides the condensation with HFPO (hexafluoropropenoxide) and the subsequent alkaline pyrolisis is necessary. No data on the above indicated properties are reported. With regard to this see Patent application USP 5,910,552.

Patent USP 3,896,179 relates to the separation of "primary" isomers of perfluorovinyl ethers, for example of $CF_3CF_2CF_2OCF=CF_2$ from the corresponding less stable "secondary" isomers $CF_3(CF_3)CFOCF=CF_2$. The latter are undesired products as regards both the polymer preparation and the poor properties of the obtained polymers.

Patent USP 4,340,750 relates to the preparation of perfluorovinyl ethers having the formula

$$CF_2=CFOCF_2R^\circ_fX^1$$

wherein R°_f is a C_1-C_{20} perfluoroalkyl optionally containing oxygen, X^1=H, Cl, Br, F, COOR$^\circ$, CONR$^\circ$R' wherein R$^\circ$ is a C_1-C_{10} alkyl group and R' represents H or a C_1-C_{10} alkyl group. In the preparation of these compounds an acylfluoride together with iodine and tetrafluoroethylene is used, avoiding the

final step of the acylfluoride pyrolisis which comes from the perfluoro-propene epoxide, by a deiodofluorination reaction, which takes place with low yields.

Patent USP 4,487,903 relates to the preparation of fluoroelastomeric copolymers (i.e., elastomeric fluoropolymers) using perfluorovinyl ethers having the formula:

$$CF_2=CF(OCF_2CFY^0)_{n^0}OX^2$$
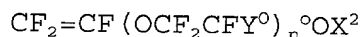
wherein n^0 ranges from 1 to 4; $Y^0=F$, Cl, CF_3, H; X^2 can be C_1-C_3 perfluoroalkyl group, C_1-C_3 ω-hydroperfluoroalkyl group, C_1-C_3 ω-chloroperfluoroalkyl group. The polymer has a content of fluorovinyl ether units ranging from 15 to 50% by moles. These vinyl ethers give copolymers which at low temperatures have better properties than those of the above mentioned perfluorovinyl ethers PVE (perfluoropropyl vinyl ether) and MVE type. In the patent it is disclosed that in order to have good properties at low temperature, the presence of at least two ether bonds in the side chain adjacent to the double bond is required. Furthermore from the patent it results that for values higher than 4 it is difficult to purify   the monomers and the effect on the decrease of the polymer T_g is lower. Besides the reactivity of the described vinyl ethers is very low and it is difficult to obtain polymers having a high molecular weight able to give good elastomeric properties. A TFE/perfluorovinyl ether copolymer ($n^0=2$) 73/27 % by moles with Tg of -32°C is exemplified. However the polymer is obtained with very long reaction times (96 hours of polymerization).

Patent EP 130,052 describes the perfluoro(vinyl polyether) (PVPE) polymerization which leads to amorphous perfluoropolymers with a T_g ranging from -15 to -100°C. The described polymers have T_g values reaching up to -76°C; the further T_g decrease is obtained by using perfluoropolyethers as plasticizers. In the patent copolymers and terpolymers of TFE and MVE with vinylethers (PVPE) having the formula

$$CF_2=CFO(CF_2CF(CF_3)O)_{n'''}R^\circ_f,$$
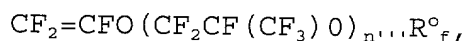
are described, wherein n''' ranges from 3 to 30 and R°_f, is a perfluoroalkyl group. Due to purification difficulties, the used vinyl ethers are vinylether mixtures with different n''' values. According to said patent the most evident effect on the T_g decrease is shown when n' is equal to or higher than 3, preferably higher   than 4. According to the polymerization examples described in said patent the final mass of the polymer, besides the hot and under vacuum treatment, must then be washed with freon® TF in order to remove all the unreacted monomer (PVPE). From the Examples it results that the reactivity of all the described monomers (PVPE) is poor.

Patent USP 4,515,989 relates to the preparation of new intermediates for the fluorovinyl ether synthesis. According to the patent the vinylether synthesis is improved by using an intermediate able to more easily decarboxylate. For its preparation fluoroepoxides of formula:

$$X^3CF_2-CF-CF_2 \quad \text{wherein } X^3 = Cl, Br$$
$$\diagdown \diagup$$
$$O$$
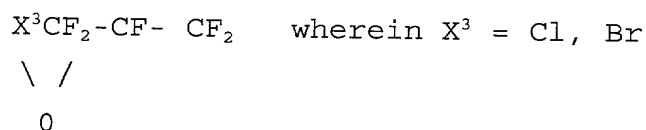
are used.

Patent USP 4,619,983 describes the copolymerization of VDF with vinyl ethers having the formula:

$$CF_2=CFOX^4$$
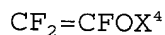
wherein X^4 is a C_3-C_9 oxyperfluoroalkyl radical containing from 1 to 3 oxygen atoms. The obtained polymers are not perfluori- nated polymers and show a poor stability to alcohols.

Patent USP 4,766,190 relates to the polymerization of perfluorovinylpolyethers (PVPE) similar to those of USP 4,487,903 with TFE and low perfluoropropene percentages, in order to increase the mechanical properties of the obtained polymers.

Patent EP 338,755 relates to the preparation of perfluorinated copolymers by using direct fluorination of partially fluorinated copolymers. More reactive partially fluorinated monomers are used, subjecting the obtained polymers are fluorinated with elemental fluorine. The fluorination step requires a supplementary process unit, besides in this step elemental fluorine is used, which is a highly oxidizing gas, with the consequent precautions connected to its use. Besides in the patent it is stated that in order not to compromise the fluorination reaction and the properties of the obtained polymer, using the invention process the percentage of the comonomer in the polymer cannot exceed 50% by moles.

Patent USP 5,268,405 reports the preparation of perfluorinated rubbers having a low Tg, by the use of high viscosity perfluoropolyethers as plasticizers of perfluorinated rubbers (TFE/MVE copolymers). However during the use perfluoropolyether bleeds take place. This is true especially for the PFPE having a low molecular weight (low viscosity): in said patent, therefore, the high viscosity PFPE use is suggested, and therefore the low viscosity PFPEs must previously be removed from these last.

Patent USP 5,350,497 relates to the preparation of perfluoroalkyl vinyl ethers by fluorination with elemental fluorine of hydrofluorochloroethers and subsequent dechlorination.

Patent USP 5,401,818 relates to the prepartion of perfluorovinyl ethers of formula:

$$R^1_f (OCF_2CF_2CF_2)_m, -OCF=CF_2$$
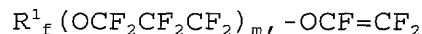
(wherein R^1_f is a C_1-C_3 perfluoroalkyl radical and m, is an integer ranging from 1 to 4) and of the corresponding copolymers having improved properties at low temperature. The preparation of said perfluorovinyl ethers is carried out by 7 steps, some of them have very low yields, and comprise also a fluorination with elemental F_2. The reactivity of said

perfluorovinyl ethers is anyhow low.

As it is shown from the above prior art, the
perfluorovinyl ether synthesis generally involves a multistep
process with low yields (USP 3,132,123, USP 3,450,684), with
additional purifications to remove undesired isomers (USP
3,896,179) and the need to control the undesired hydrogenated
by-products (USP 3,291,843). Alternatively, in the synthesis
substances acting as intermediates, which are suitably
prepared, and which allow to eliminate said drawbacks (USP
4,340,750, USP 4,515,989), are used.

Furthermore in some cases the vinylether preparation
requires the fluorination with elemental fluorine of partially
fluorinated intermediates (USP 5, 350,497); or, to avoid
synthesis and low reactivity problems of the perfluorovinyl
ethers, fluorination of partially fluorinated polymers (EP
338,755) is suggested.

Other problems shown in the prior art relate to the low
reactivity of the perfluorovinyl ethers, which makes it
necessary the recovery of the unreacted monomers from the
reaction raw products (English Patent UK 1,514,700), and the
stability problems for the polymers having -C(O)F end groups
(USP 3,635,926). These last can be furtherly transformed by
suitable reactants in order to increase the stability of the
fluorinated polymer (EP 178,935).

Perfluoro(oxyalkyl vinyl ethers) are used to confer to
the fluorinated rubbers good properties at low temperatures,
and specifically to lower the copolymer glass transition
temperature.

By increasing the perfluorooxyalkyl units forming the
side perfluorooxyalkyl substituent, the T_g of the corresponding
obtainable amorphous copolymers decreases, but at the same
time the vinylether reactivity drastically decreases, making
more evident the problems previously shown for the recovery of
the unreacted monomer from the raw polymerization products or
from the polymer itself (USP 4,487,903 - EP 130,052). In some

cases, where the monomer cannot be completely removed by simple stripping under vacuum, more washings must then be carried out with fluorinated solvents for completely eliminating the unreacted vinyl ethers from the polymeric mass.

The perfluoromethylvinylether (MVE) is used as comonomer in plastomeric fluoropolymers and, at higher concentrations, also in elastomeric fluoropolymers. In particular in, EP 633,257 and EP 633,274 MVE is polymerized with TFE in the presence of small amounts of PVE or dioxoles to obtain polymers with improved flex life.

The amorphous copolymers of TFE with perfluoromethyl-vinylether have a T_g around 0°C or slightly lower (Maskornik, M. et al. "ECD-006 Fluoroelastomer - A high performance engineering material". Soc. Plast Eng. Tech. Pao. (1974), 20, 675-7).

The T_g extrapolated value of the MVE homopolymer is of about -5°C (J. Macromol. Sci.-Phys., B1(4), 815-830, Dec. 1967).

In Patents USP 5,296,617 and 5,235,074 there is described the hypofluorite $CF_2(OF)_2$ reactivity towards unsaturated products, which contemporaneously leads to the formation of the dioxolane derivative and to the fluorination compound of the olefin itself. In Patent EP 683,181 there is described the $CF_2(OF)_2$ reactivity towards olefins which leads to the formation of linear reaction compounds between one hypofluorite molecule and two molecules of the same olefin, for the preparation of symmetric dienes.

The Applicant has surprisingly and unexpectedly found that it is possible to solve the above mentioned technical problems, by using special fluoro vinyl ethers that are furthermore easily synthesizable and obtainable by a continuous process.

An object of the present invention are fluorovinyl ethers of general formula:

$$CFX=CXOCF_2OR \qquad (I)$$
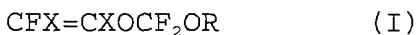
wherein R is a C_2-C_6 linear, branched or C_5-C_6 cyclic (per)fluoroalkyl group, or a C_2-C_6 linear, branched (per)fluoro oxyalkyl group containing from one to three oxygen atoms; when R is a fluoroalkyl or fluorooxyalkyl group as above defined it can contain from 1 to 2 atoms, equal to or different from each other, selected from the following: H, Cl, Br, I; X = F, H. The term (per)fluoro refers to a molecule in which from one up to all of the hydrogens capable of beign replaced with fluorine are replaced with fluorine.
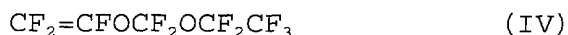
The fluorovinyl ethers of general formula:

$$CFX=CXOCF_2OCF_2CF_2Y \qquad (II)$$
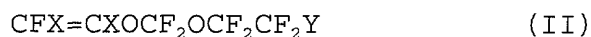
wherein Y = F, OCF_3; X as above defined, are preferred among the compounds of formula (I).

The perfluorovinyl ethers of formula:

$$CF_2=CFOCF_2OCF_2CF_2Y \qquad (III)$$
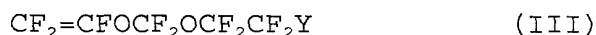
wherein Y is as above defined, are furtherly preferred. For example the perfluorovinyl ether having the formula:

$$CF_2=CFOCF_2OCF_2CF_3 \qquad (IV)$$

can be mentioned.

Surprisingly, the vinyl ethers according to the invention show the advantages reported hereinafter with respect to the known vinyl ethers.

The obtainable advantages can be attributed to the $-OCF_2O-$ unit directly bound to the ethylene unsaturation.

The Tg lowering obtained with the vinyl ethers of the invention is connected to the presence of the ($-OCF_2O-$) unit directly bound to the unsaturation. The Tg lowering is surprisingly so evident to be defined a primary effect.

In fact if the vinylether of the invention with two oxygen atoms is used:

$$CF_2=CF-O-CF_2-O-CF_2CF_3 \qquad (MOVE\ 1)$$
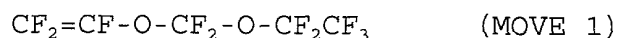
the Tg lowering is clearly higher with respect to the Tg of the polymer from PVE

$$CF_2=CF-O-CF_2CF_2CF_3 \qquad (PVE)$$
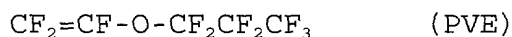
and to the vinyl ether having the same formula, but with the second oxygen atom in a different position and without showing the characteristic unit ($-OCF_2O-$)

$$CF_2=CF-O-CF_2CF_2-O-CF_3 \qquad (\beta-PDE)$$

It is surprising to notice that with respect to MVE

$$CF_2=CF-O-CF_3$$

the β-PDE vinyl ether does not give any advantage as regards Tg.
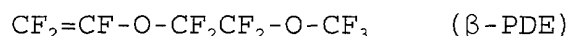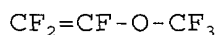
On the contrary the primary effect of the ($-OCF_2O-$) unit results very clear with the vinyl ethers of the invention (MOVE).

Besides it has surprisingly been found that the ($-OCF_2O-$) unit bound to the ethylene unsaturation of the vinyl ethers of the invention increases the vinylether reactivity drastically reducing the rearrangements to $C(O)F$ which cause instability.

The advantages of the polymers of the invention can be summarized as follows:

- The reactivity of the new monomers allows to prepare copolymers having a high MW (molecular weight) with a very low content of carboxylic groups or derivatives thereof such as $-C(O)F$, $-COO-$. The carboxylic group content in the copolymer of a monomer of the present invention with TFE has resulted of about 10 times lower than that of a copolymer prepared under the same conditions but using perfluoropropyl vinyl ether (PVE) instead of fluorovinyl ethers (see the Examples). As said, the presence of a lower content of carboxylic groups, or of the corresponding derivatives (amides, esters, etc.) results in more stable polymers.
- The reactivity of the monomers of the invention is surprisingly high (see the homopolymerization Examples). The fluorovinyl ethers of the invention can be used as comonomers both in plastomeric (per)fluoropolymers

(containing crystalline domains) and in elastomeric
(per)fluoropolymers. To obtain plastomeric polymers the
amount of the vinylether of the invention must be such to
allow and lead to the formation of crystalline domains,
generally < 10% by moles. The presence of crystalline
domains can be determined by DSC. To obtain amorphous
polymers the amount of the vinylether of the invention
must be such to lead to the disappearance of the
crystalline domains. The skilled man in the art can
easily find the amount of the vinylether of the invention
which is required for obtaining said results.
The novel fluorovinyl ethers of the present invention can
be used in amounts as low as about 0.1 % on a mole basis.
Generally the amount of the vinyl ether for obtaining
amorphous polymers is higher than 10% by moles (i.e. 10
mole %), preferably in the range from about 15 to 20% by
moles, or higher. In the case of copolymers having a high
content of vinyl ether monomer, the properties at low
temperature (T_g) of the polymers of the invention result
clearly better with respect both to copolymers having the
same MVE content (see the Examples) and also,
surprisingly, with respect to copolymers where the
perfluorovinyl ether, the oxygen atoms being equal, does
not show the -OCF$_2$Ogroup directly bound to the
unsaturation, as in the case of the $CF_2=CFOCF_2CF_2OCF_3$ (β-
PDE) (see the Examples).
- Their use in the polymerization reactions with fluoroo-
lefins allows to substantially and contemporaneously
reduce two important disadvantages of the prior art: the
recovery of the unreacted vinylether and the polymer
instability due to the presence of carboxylic end groups.
A further advantage of the fluorovinyl ethers of the
invention, as hereinafter illustrated, consists in that
their preparation is carried out in a continuous plant by
a limited number of steps. Furthermore the used raw

materials are inexpensive. The following raw materials can for example be mentioned:

$CF_2(OF)_2$, $CF_2=CF_2$, $CF_2=CFOCF_3$, CHCl=CFCl, CFCl=CFCl, $CF_2=CFCl$, $CF_2=CFH$, $CF_2=CH_2$, CHCl=CHCl and other olefins. The use of these reactants is specified in the synthesis process of the vinyl ethers of the invention.

When used in connection with a quantity the term about refers to such normal variation in that quantity as would be expected by the skilled artisan.

As used herein, essentially free of crystalline zones or regions means that crystallinity is not detected by, for example, DSC, under typical ordinary conditions as would be used by the skilled artisan in routine experiments.

Polymers, homopolymers and copolymers are obtainable by polymerizing the fluorovinyl ethers of general formula (I) - (IV) alone or with at least another monomer.

With copolymer, a polymer containing the vinyl ether of the invention and one or more comonomers, is meant.

Preferred comonomers are fluorinated compounds having at least one polymerizable double bond C=C, optionally containing hydrogen and/or chlorine and/or bromine and/or iodine and/or oxygen.

Other comonomers that can be copolymerized withn the fluorovinyl ethers of the present invention are non fluorinated C_2-C_8 olefins, i.e. olefinically unsulated hydrocarbons such as ethylene, propylene, isobutylene.

Among the usable comonomers the following can be mentioned:

- C_2-C_8 perfluoroolefins, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP), hexafluoroisobutene;
- C_2-C_8 hydrogenated fluoroolefins, such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, $CH_2=CH-R^2_f$ perfluoroalkylethylenes, wherein R^2_f is a C_1-C_6 perfluoroalkyl group;

- C$_2$-C$_8$ chloro- and/or bromo- and/or iodo-fluoroolefins, such as chlorotrifluoroethylene (CTFE) and bromotri-fluoroethylene;

- CF$_2$=CFOR^2_f (per)fluoroalkyl vinyl ethers (PAVE), wherin R^2_f is a C$_1$-C$_6$ (per)fluoroalkyl group, for example a trifluoromethyl, bromodifluoromethyl or a heptafluoropropyl group;

- CF$_2$=CFOX^a (per)fluoro-oxyalkylvinyl ethers, wherein X^a is: a C$_1$-C$_{12}$ alkyl, or a C$_1$-C$_{12}$ oxyalkyl group, or a C$_1$-C$_{12}$ (per)fluorooxyalkyl group having one or more ether groups, for example perfluoro-2-propoxypropyl.

- sulphonic monomers having the structure CF$_2$=CFOX^{b}SO$_2$F, wherein X^b = CF$_2$CF$_2$, CF$_2$CF$_2$CF$_2$, CF$_2$CF(CF$_2$X^c) wherein X^c = F, Cl, Br.

The process for preparing fluorinated polymers according to the present invention can be carried out by polymerization in organic solvent as described in United States Patents 4,864,006 and 5,182,342, herein incorporated by reference. The organic solvent is selected from the group including chlorofluorocarbons, perfluoropolyethers, hydrofluorocarbons and hydrofluoroethers.

The process for preparing the polymers of the present invention can be carried out also by polymerization in aqueous emulsion according to well known methods in the art, in the presence of a radical initiator which can be selected for example from: inorganic peroxides (for example alkaline metal or ammonium persulphates, perphosphates, perborates or percarbonates), optionally in combination with ferrous, cuprous or silver salts, or of other easily oxidizable metals; organic peroxides (for example, disuccinylperoxide, terbutyl-hydroperoxide, diterbutylperoxide); azocompounds (see USP 2,5-15,628 and USP 2,520,338, herein incorporated by reference). It is also possible to use organic or inorganic redox systems, such as ammonium persulphate/sodium sulphite, hydrogen peroxide/aminoiminomethansulphinic acid to mentioned just a

few.

In the reaction medium also surfactants of various type are usually present, among which the fluorinated surfactants of formula:

$R^3_f-X^-M^+$
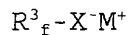
are particularly preferred, wherein R^3_f is a C_5-C_{16} (per)fluoro-alkyl chain or a (per)fluoropolyoxyalkyl chain, X^- is $-COO^-$ or $-SO_3^-$, M^+ is selected from: H^+, NH_4^+, an alkaline metal ion. Among the most commonly used, ammonium perfluorooctanoate, (per)fluoropolyoxyalkylenes ended with one or more carboxylic groups, etc. can be mentioned.

During the polymerization, known iodinated a brominated chain transfer agents can be added to the reaction medium. It is also possible to use as chain transfer agents alkaline or earthalkaline metal iodides or bromides, according to United State Patent 5,173,553, herein incorporated by reference.

Other chain transfer agents are mentioned in United States Patent 4,766,190, herein incorporated by reference.

The crosslinking process of the amorphous polymers of the present invention can be carried out according to methods well known in the art. When, for example, one of the comonomers is vinylidene fluoride or vinyl fluoride, curing can be carried out with polyamines or aromatic polyols in the presence of suitable catalysts (accelerants) as described in United State Patent 3,876,654, United State Patent 4,259,463; when the monomer is perfluorinated, one generally uses in the copolymerization in amounts lower than or equal to 3%, a comonomer having a reactive site formed, for example, by Br, I, CN, OC_6F_5, $COOR^a$ wherein R^a is an alkyl from 1 to 5 carbon atoms, or by double bonds as described in United State Patent 5,268,405; when the polymer contains Br or I, it is cured in the presence of a peroxide or of a polyunsaturated compound as described in United State Patents 4,948,852, 4,948,853 and 4,983,60, EP 683,149.

Another object of the present invention consists in the

synthesis process of the new (per)fluorovinyl ethers, which comprises the reaction of hypofluorite $CF_2(OF)_2$ fluorinated olefin of formula $R_1R_2C=CR_3R_4$ to give a first intermediate hypofluorite $F-CR_1R_2-CR_3R_4-OCF_2OF$, the subsequent reaction of said compound with a second fluorinated olefin of formula $R_5R_6C=CR_7R_8$ to give second intermediate $F-CR_1R_2-CR_3R_4-OCF_2O-CR_5R_6--CR_7R_8-F$, which by an elimination reaction such as dehalogenation or dehydrohalogenation leads to the new perfluorovinyl ethers.

The general scheme of the synthesis is the following:

a) $CF_2(OF)_2 + R_1R_2C=CR_3R_4 \rightarrow F-CR_1R_2-CR_3R_4-OCF_2OF$ (VI)

b) $F-CR_1R_2-CR_3R_4-OCF_2OF + R_5R_6C^2=C^1R_7R_8 ------ \rightarrow$

    $F- CR_1R_2-CR_3R_4-OCF_2O-C^2R_5R_6-C^1R_7R_8-F$ (VII)

    dehalogenation./

c) $F-CR_1R_2-CR_3R_4-OCF_2O-C^2R_5R_6-C^1R_7R_8-F ------ \rightarrow$,

    /dehydrohalogenation.

    $CFX=CXOCF_2OR$ (I)
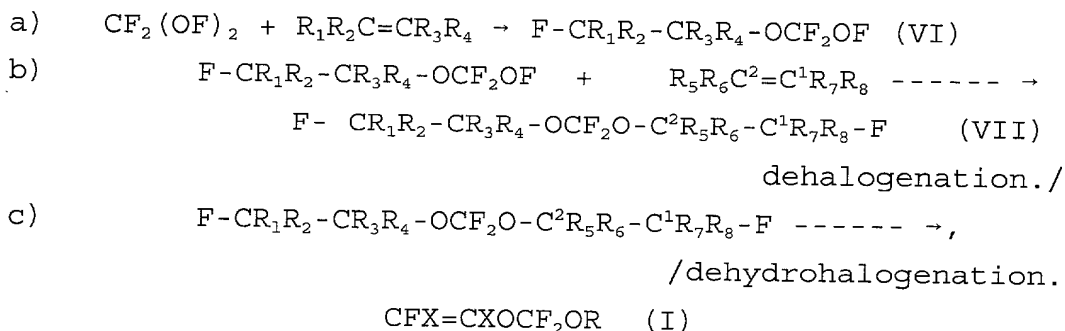
In this synthesis scheme:

- with reference to the formula of the compound (VII):
  - R_1, R_4, are the same or different and are H, F; R_2, R_3, are the same or different and are H, Cl under the following conditions: (1) when the final reaction is a dehalogenation, R_2 R_3 = Cl; (2) when the final reaction is a dehydrohalogenation one of the two substituents R_2, R_3 is H and the other is Cl;
  - R_5, R_6, R_7, R_8 are :
    - F, or one of them is a C_1-C_4 linear or branched perfluoroalkyl group, or a C_1-C_4 linear or branched perfluorooxyalkyl group containing from one to three oxygen atoms, or R_5 and R_7, or R_6 and R_8, are linked each other to form with C^2 and C^1 a C_5-C_6 cycle perfluoroalkyl group;
    - when one of the R_5 to R_8 radicals is a C_2-C_4 linear or branched fluoroalkyl, or a C_2-C_4 linear or branched fluorooxyalkyl group

containing from one to three oxygen atoms, one
or two of the other R_5 to R_8 are F and one or
two of the remainders, equal to or different
from each other, are selected from H, Cl, Br,
Iodine; when the substituents selected from H,
Cl, Br, Iodine are two, they are both linked to
the same carbon atom; when R_5 and R_7, or R_6 and
R_8, are linked each other to form with C^2 and C^1
a C_5-C_6 cycle fluoroalkyl group, one of the two
free substituents R_6, R_8 or R_5, R_7 is F and the
other is selected from H, Cl, Br, Iodine.

-    the fluoroalkene used in the reaction a) is replaceable
    with that of the subsequent reaction b); in this case the
    meanings defined for the substituents of the R_1-R_4 group,
    and respectively of the R_5-R_8 group, are interchangeable
    each other, with the proviso that the position of each
    radical of each of the two groups R_1-R_4 and R_5-R_8 with
    respect to -OCF_2O- on the chain of the intermediate
    compound (VII), is the same which is occupied if the
    synthesis takes place according to the above reported
    scheme and the two olefins each react in the considered
    steps.

In the first reaction a) of the above illustrated scheme
a hypofluorite gas flow $CF_2(OF)_2$, optionally suitably diluted
with an inert fluid, comes into contact (i.e is contacted
with), in a suitable reactor with outlet, on the bottom of the
same (first reactor), with the $R_1R_2C=CR_3R_4$ olefin, optionally
diluted in an inert fluid and preferrably in gas flow, to
allow the chemical reaction a) with formation of the
intermediate hypofluorite (VI). To favour the reaction
stoichiometry, the reactants must be introduced into the
reactor in an approximately unitary molar ratio, or with an
excess of $CF_2(OF)_2$. The residence time of the mixture in the
reactor can range from about a few hundredths of second up to
about 120 seconds depending on the olefin reactivity, the

reaction temperature, and the presence of optional reaction solvents.

The reaction temperature can range from about -40° to about -150°C, preferably from about -80° to about -130°C.

The compound (VI) usually is not separated from the reaction product and it is transferred in a continuous way to the subsequent reaction described in step b).

The mixture of the products coming out from the first reactor can be heated at room temperature before being fed into the second reactor.

In the second reaction b), the second olefin $R_5R_6C=CR_7R_8$ pure or in solution, reacts with the product obtained in the first reaction with formation of compound (VII).

The olefin can be fed in a continuous way, so as to maintain its concentration constant in the reactor; except for normal variation as would be expected by the skilled asrtisan. The temperature of the reaction b) can range from about -20° to about - 130°C, preferably from about -50° to about -100°C. The olefin concentration is higher than or equal to about 0.01M, preferably the concentration is higher than 3M, more preferably also the compound in a highly purified state can be used.

The solvents used in steps a) and b) are perfluorinated or chlorohydrofluorinated solvents or hydrofluorocarbons. Examples of said solvents are:
CF_2Cl_2, $CFCl_3$, CF_3CFH_2, $CF_3CF_2CF_3$, CF_3CCl_2H, CF_3CF_2Cl.
In the reaction c) the compound (VII), dependently on the olefins used in steps a) and b), after distillation from the reaction product, is subjected to dechlorination or to dehydrochlorination to obtain the vinyl ethers of formula (I). This last step can be carried out by using reactions widely described in the prior art. The suitable selection of the substituents R_1 to R_8 in the two olefins used in the synthesis allows to obtain the vinyl ethers of the present invention.

Another object of the invention is a process wherein a

hypofluorite of formula $X_1X_2C(OF)_2$ wherein X_1 and X_2 equal or different are F, CF_3, and two   fluoroalkenes of formula respectively $R^A_1R^A_2C=CR^A_3R^A_4$ and $R^A_5R^A_6C=CR^A_7R^A_8$, wherein R^A_1-R^A_8 equal or different, are F, H, Cl, Br, I, $-CF_2OSO_2F$, $-SO_2F$, $-C(O)F$, C_1-C_5 linear or branched perfluoroalkyl or oxyperfluoroalkyl group, are reacted according to steps a) and b), excluding the dehalogenation or dehydrohalogenation step, to obtain compounds of general formula (VIII)

$F-CR^A_1R^A_2-CR^A_3R^A_4-OCF_2O-CR^A_5R^A_6-CR^A_7R^A_8-F$.
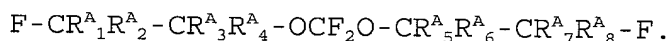
The following Examples are reported with the purpose to illustrate the invention and they do not limit the scope of the same.

In the Examples the thermogravimetric analysis TGA is carried out by using a 10°C/min rate.

EXAMPLE 1

Synthesis of $CF_3CF_2OCF_2OCFClCF_2Cl$ perfluoro-1-2,dichloro-3,5-dioxaheptane.

The reactor used is of the cylindrical type, with a total volume of about 300 ml and is equipped with magnetic dragging mechanical stirrer, turbine with recycle of the reacting gas placed at 20 cm from the reactor top, internal thermocouple, two internal copper pipes for the reactant feeding which end at about 1 mm from the turbine, and product outlet from the bottom. In the reactor, inside of which the temperature is maintained at -114°C, 1.1 1/h (litres/hour) of $CF_2(OF)_2$ and 3.3 1/h of He are introduced through one of the two inlet pipes; A flow of 1.1 1/h of $CF_2=CF_2$ and 0.7 1/h of He is maintained through the second inlet pipe. Feeding is continued for 6.6 hours.

The residence time of the transport gas in the reaction zone comprised between the outlet of the two feeding pipes in the reactor and the inlet of the discharge pipe is of about 4 sec.

On the reactor bottom the reaction products are brought

The reactor used is of the cylindrical type, with a total volume of about 300 ml and is equipped with magnetic dragging mechanical stirrer, turbine with recycle of the reacting gas placed at 20 cm from the reactor top, internal thermocouple, two internal copper pipes for the reactant feeding which end at about 1 mm from the turbine, and product outlet from the bottom. In the reactor, inside of which the temperature is maintained at -114°C, 1.1 l/h (litres/hour) of $CF_2(OF)_2$ and 3.3 l/h of He are introduced through one of the two inlet pipes; A flow of 1.1 l/h of $CF_2=CF_2$ and 0.7 l/h of He is maintained through the second inlet pipe. Feeding is continued for 6.6 hours.

The residence time of the transport gas in the reaction zone comprised between the outlet of the two feeding pipes in the reactor and the inlet of the discharge pipe is of about 4 sec.

On the reactor bottom the reaction products are brought to room temperature and the gaseous mixture flow, monitored by gas chromatography, is fed in a continuous way, under mechanical stirring, into a second reactor having a 250 ml volume maintained at the temperature of -70°C, equipped with mechanical stirrer, thermocouple, dipping inlet for the reacting mixture, outlet with head of inert gas. The reactor contains 72.6 g of dichlorodifluoroethylene CFCl=CFCl.

At the end of the addition of reacting gases into the second reactor, the reaction raw material is distilled by a plate column at atmospheric pressure, collecting 41.5 g of the desired product (boiling point 91°C).

The yield of perfluoro-1,2 dichloro-3,5-dioxaheptane, calculated with respect to $CF_2(OF)_2$, is of 36%.

Characterization of perfluoro 1,2, dichloro-3,5-dioxaheptane.

Boiling point at atmospheric pressure: 91°C.

^{19}F-NMR spectrum in p.p.m. (with respect to $CFCl_3$ at 0):

$CF_2=CF-OCF_3$ and 0.7 1/h of He for 4.5 hours.

The residence time of the transport gas in the reaction zone comprised between the reactor outlet and the end of the two feeding pipes is of about 3 sec.

On the reactor bottom the reaction products are brought to room temperature and the gaseous mixture flow, monitored by gas chromatography, is fed in a continuous way, under mechanical stirring, into a second reactor identical to the one used for the same step in Example 1. Inside, where a temperature of -70°C is maintained, there are 51 g of dichlorofluoroethylene $CFCl=CFCl$.

At the end of the addition of the reacting gases into the second reactor, the reaction raw material is distilled by a plate column at the reduced pressure of 250 mmHg. 50 g of a mixture formed by two isomers, respectively, isomer A) perfluoro-1,2-dichloro-3,5,8-trioxanonane and isomer 3) perfluoro-1, 2-dichloro-3, 5, 7-trioxa-6-methyloctane are collected. The mixture composition is determined by gas chromatography and is the following: isomer A 79%, isomer B 21%. The molar yield of A+B with respect to the used $CF_2(OF)_2$ is 38%. The molar yield of A+B with respect to the used perfluoromethylvinylether is 42%. The isomers have been separated by preparative gas chromatography.

Characterization of products A and B

Mixture boiling point (A 79%, B 21%) at the reduced pressure of 250 mmHg: 82°C.

^{19}F-NMR spectrum in p.p.m. (with respect to $CFCl_3$ at 0) of the isomer A:

-50.6/-52.4 (2F, $O-CF_2-O$);   -70.0/-71.8 (2F, $C-CF_2Cl$);
-77.7 (1F, O-CFCl-C);   -55.3/-55.6 (3F, CF_3-OC);
-90.7/-91.1 (2F, $C-OCF_2-C$); -90.2/-90.6 (2F, $C-OC-CF_2OCOC$).

^{19}F-NMR spectrum in p.p.m. (with respect to $CFCl_3$ at 0) of isomer B:

-50.0/-52.1 (2F, $O-CF_2-O$)   -70.0/-71.8 (2F, $C-CF_2Cl$);

-77.9 (1F, O-CFCl-C);   -54.6/-54.9 (3F, CF$_3$OC):

-85.7/-86.1 (3F, OC (CF$_3$)0);   -100.3/-101.0 (1F,OCF(C)O).

Mass spectrum (electronic impact) main peaks and respective intensities:

Product A: 69 (50); 119 (100); 151 (50); 185 (42); 251 (38);

Product B: 69 (96); 97 (50); 135 (42); 151 (92); 185 (100).

IR spectrum (cm^{-1}), intensity of the mixture A 79%, B 21%:

(w)=weak, (m)=medium, (s)=strong, (vs)=very strong:

1388 (w); 1288 (vs); 1233 (vs); 1151 (vs); 1104 (vs); 1032

(s); 846 (m); 685 (w)

EXAMPLE 3

Synthesis of CF$_3$OCF$_2$CF$_2$OCF$_2$OCHClCHFCl perfluoro-1,2-dichloro-
1,2-dihydro-3,5,8-trioxanonane (isomer C) and
CF$_3$OCF(CF$_3$)OCF$_2$OCHClCHFCl perfluoro-1,2-dichloro-1,2-dihydro-
3,5,7-trioxa-6-methyloctane (isomer D).

In a reactor identical to that used in Example 1,
maintained at the temperature of -112°C, 1.55 l/h of CF$_2$(OF)$_2$
and 4.5 l/h of He are introduced through one of the two inlet
pipes; through the second inlet pipe 1.4 l/h of CF$_2$=CF-OCF$_3$ and
0.7 l/h of He for 5 hours.

The residence time of the transport gas in the reaction
zone comprised between the reactor outlet and the end of the
two feeding pipes is about 3 sec.

On the reactor bottom the reaction products are brought
to room temperature and the gaseous mixture flow, monitored by
gas chromatography, is fed in a continuous way, under mecha-
nical stirring, into a second reactor identical to the one
used for the same step in Example 1. Inside, the temperature
is of -70°C and there are 50 g of 1,2-dichloroethylene
CClH=CClH and 50 g of CFCl$_3$.

At the end of the addition of the reacting gases into the
second reactor, after distillation of the solvent at room
pressure, the reaction raw material is distilled by a plate
column at the reduced pressure of 100 mmHg. 43.5 g of the mi-

xture of the desired products (isomer C 78%, isomer D 22W, determined by gaschromaography) are collected. The molar yield of C+D with respect to the used $CF_2(OF)_2$ is 33%. The isomers have been separated by preparative gas chromatography.

Characterization of products C and D

Mixture boiling point (C 78%, D 22%) at the reduced pressure of 100 mmHg: 71°C.

^{19}F-NMR spectrum in p.p.m. (with respect to $CFCl_3$ at 0) of the isomer C perfluoro-1,2-dichloro-1,2-dihydro-3,5,8-trioxanonane:

-56. 0/-57.2 (2F, $O-CF_2-O$); -143.2/-146.0 (1F, C- CHFCl); -55.8 (3F, CF_3-OC);   -91.0/-91.4 (2F, $C-OCF_2-C$); -90.3/-90.5 (2F, $C-OC-CF_2OCOC$).

^{19}F-NMR spectrum in p.p.m. (with respect to $CFCl_3$ at 0) of the isomer D perfluoro-1,2-dichloro-1,2-dihydro-3,5, 7-trioxa-6-methyloctane:

-56.0/-57.2 (2F, $O-CF_2-O$); -143.2/-146.0 (1F, C-CHFCl); -54.9/-55.1 (3F, CF_3-OC); -86.2/-86.3 (3F, $OC(CF_3)0$); -100.5/-101.0 (1F, OCF(C)O).

^{1}H spectrum in p.p.m. (with respect to TMS) of the isomers C and D: 6.28/6.05 (1H -CHFCl); 6.02/5.95 (1H -CHCl-)

Mass spectrum (electronic impact), main peaks and respective intensities %:
69 (84); 119 (100); 185 (51.1); 251 (84); 281 (15.8); 283 (4.8); 347 (5.7); 349 (1.7).

IR spectrum (cm^{-1}) intensity : (w)=weak, (m)=medium, (s)=strong, (vs)=very strong:
3001.0 (w); 2920.9 (w); 2850.9 (w); 1286.3 (vs); 1233.7 (vs); 1125.5 (vs); 1081.8 (s); 1047.9 (s); 815.9 (m); 766.3 (m).

EXAMPLE 4

Dehalogenation of perfluoro 1,2-dichloro-3,5-dioxaheptane

In a 25 ml three-necked flask, equipped with mechanical stirrer, thermometer, dropping funnel, distillation column

equipped with water refrigerant and collecting trap maintained at -78°C and connected to a mechanical vacuum pump, 150 ml of DMF, 15 g of poudered Zn in powder, 0.5 g of K_2CO_3 and 100 mg of I_2 are introduced. The internal temperature is brought to 80°C and 50 g of perfluoro -1,2-dichloro-3,5-dioxaheptane are added dropwise. When the addition is over the mixture is allowed to react for about 30 minutes. At the end the internal pressure gradually brought from starting 760 mmHg to 300 mmHg. After about 20 minutes the collecting trap containing 34.2 g of perfluoro-3,5-dioxa-1-heptene (MOVE 1) is disconnected.

The dehalogenation yield is 85%.

Characterization of perfluoro-3,5-dioxa-1-heptene (MOVE 1)

Boiling point at atmospheric pressure: 41.9°C.

^{19}F-NMR spectrum in p.p.m. with respect to $CFCl_3$ at 0:

-56.8 (2F, $O-CF_2-O$);   -87.2 (3F, CF_3-C);

-90.6 (2F, $C-CF_2-O$);   -114 (1F, O-C=C-F);

-121.8 (1F, O-C=CF);   -137 (1F, O-C-F=C);

Mass spectrum (electronic impact), main peaks and respective intensities:

69 (66.5%); 119 (100%); 147 (83.4%); 185 (89.4%); 216 (67.3%); 282 (8.2%).

IR spectrum (cm^{-1}) intensity: (w)=weak, (m)=medium, (s)=strong, (vs)=very strong:

1839.5 (m); 1407.6 (w); 1307.4 (vs); 1245.8 (vs); 1117.4 (vs); 907.2 (m); 846.0 (m).

EXAMPLE 5

Dehalogenation of the isomer mixture A+B obtained in Example 2 (perfluoro-1,2-dichloro-3,5,8-trioxanonane $CF_3OCF_2CF_2CF2OCFClCF_2Cl$ + perfluoro-1,2-dichloro-3,5,7-trioxa-6-methyloctane $CF_2OCF(CF_3)OCF_2OCFClCF_2Cl$).

In a 250 ml flask equipped as described in the previous Example 4, 110 ml of DMF, 10 g of Zn in powder and 0.3 ml of Br_2 are introduced. The internal temperature is brought to 75°C

and 30.3 g of the binary mixture A+B separated in the previous Example 2 are added drop by drop. when the addition is over the mixture is allowed to ract for about 3 hours. At the end the internal pressure is gradually lowered from 760 mmHg to 200 mmHg at -79°C. After about 30 minutes the collecting trap is disconnected. The corresponding content, which is washed with water, is recovered. At the end 24.0 g of a mixture formed for 79% (gas chromatographic determination) by perfluoro-3,5,8-trioxa-1-nonene (MOVE '2) $CF_3OCF_2CF_2OCF_2OCF=CF_2$ (isomer A') and for 21% by perfluoro-3,5,7-trioxa-6,methyl-1 octene (MOVE 2a) $CF_3OCF(CF_3)OCF_2O-CF=CF_2$ (isomer B') are obtained, which are then separated by preparative gas chromatography.

Characterization of products A' and B'

Boiling range of the isomer mixture at atmospheric pressure: 72.5°-74.5°C.

^{19}F-NMR spectrum in p.p.m. (with respect to $CFCl_3$ at 0) of the isomer A':
-55.9 (3F, CF_3-O); -56.9 (2F, O-CF_2-O); -90.8 (2F, C-CF_2-O); -91.2 (2F, O-CF_2-C); -114 (1F, O-C=C-F); -121.8 (1F, -O-C=CF); -137 (1F, O-CF=C)

^{19}F-NMR spectrum in p.p.m. (with respect to $CFCl_3$ at 0) of the isomer B':
-55.9 (3F, CF_3-O); -56.2 (2F, O-CF_2-O); -86.4 (3F, CF_3-C); -100.9 (1F, CF; -114 (1F, O-C=C-F); -122 (1F, O-C=CF); -137 (1F, O-CF=C).

Mass spectrum (electronic impact), main peaks and respective intensities of the isomer A':
69 (74); 81 (18); 119 (100); 147 (59); 185 (26); 251 (21);

Mass spectrum (electronic impact), main peaks and respective intensities of the isomer B':
69 (80); 81 (37); 97 (47); 119 (36); 147 (100); 185 (19).

IR spectrum (cm^{-1}) intensity: (w)=weak, (m)=medium, (s)=strong, (vs)=very strong, 1839 (m); 1343 (s); 1248 (vs); 1145 (vs); 918 (m); 889 (m).

EXAMPLE 6

Dehalogenation of the isomers C+D mixture obtained in Example 3 (CF$_3$OCF$_2$CF$_2$OCF$_2$OCHClCHFCl perfluoro-1,2-dichloro-1,2-dihydro-3,5,8-trioxanonane (isomer C)+ CF$_3$OCF(CF$_3$) OCF$_2$OCHClCHFCl perfluoro-1,2-dichloro-1,2-dihydro-3,5,7-trioxa-6-methyloctane (isomer D)).

In a 500 ml three-necked flask, equipped with mechanical stirrer, thermometer, dropping funnel, distillation column having a water refrigerant and a collecting trap maintained at the temperature of -78°C, 250 ml of DMF, 30 g of zinc in powder and 300 mg of I$_2$ are introduced.

The temperature is brought to 100°C and 56.9 g of the isomer mixture obtained in Example 3 are added dropwise.

When the addition is over the reactor internal temperature is brought to 120°C and stirring is maintained for 24 hours. At the end the reaction product, which contains traces of solvent and which is collected in the trap maintained at -78°C, is distilled. After washing with water 35 g of a mixture of perfluoro-1,2-dihydro-3-5-8-trioxa-1-nonene (isomer C', 79% by moles) and of perfluoro-1,2-dihydro-3-5-7-trioxa-5-methyl-1-octene (isomer-D', 21 % by moles) are recovered. The isomers are separated by preparative gas chromatography.

The dehaloagenation reaction yield is 76%.

Characterization of products C' and D'

Boiling range of the mixture of isomers C' 79%, D' 21% at atmospheric pressure: 90.0°-92.0°C.

^{19}F-NMR spectrum in p.p.m. (with respect to CFCl$_3$ at 0) of the isomer C' perfluoro-1,2-dihydro-3,5,8-trioxa-1-nonene:
-55.7 (3F, CF$_3$-O);   -57.3 (2F, O-CF$_2$-O);
-90.9 (2F, C-CF$_2$-O);   -91.2 (2F, O-CF$_2$-C) ;
-149.3/-150.0 (1F, O-C=C-F).

^{19}F-NMR spectrum in p.p.m. (with respect to   CFCl$_3$ at 0) of the isomer D' perfluoro-1,2-dihydro-3,5,7-trioxa-6-methyl-1-octene:
-55.0 (3F, CF$_3$-0);   -56.9 (2F, O-CF$_2$-0);

-86.2 (3F, CF$_3$-C);   -101.0 (1F, CF).

-149.3/-150,0 (1F, O-C=C-F)

Mass spectrum (electronic impact), main peaks and respective intensities %:

69 (82); 119 (100); 185 (29); 246 (25); 251 (20); 312 (43).

IR spectrum (cm^{-1}) intensity of the isomer mixture (C'
79%, D' 21%): (w)=weak, (m)=medium, (s)=strong,   (vs)=very
strong:

3140 (w); 1722 (w); 1695 (w); 1402 (m); 1281 (vs); 1237 (vs);
1147 (vs); 1106 (vs); 1030 (m).

EXAMPLE 7

Homopolymerization of perfluoro-3,5-dioxa-1-heptene (MOVE 1).

In a glass reactor for polymerizations, having a 20 ml
volume, equipped with magnetic stirrer and with an inlet for
the reactant feeding and discharge, 60 µl of perfluoropropio-
nylperoxide at 3% by weight in CFCl$_2$CF$_2$Cl and 3 g of MOVE 1 are
in sequence introduced. The so charged reactor is brought to
the temperature of -196°C, evacuated, brought to room
temperature. The cooling-evacuation procedure is repeated.
At the end of the degassing operations the reactor is
thermostated at the temperature of 30°C and the mixture is
allowed to react under these conditions for two days under
magnetic stirring.

The reaction raw material which is finally recovered
appears as a slightly viscous, transparent, colourless and
homogeneous solution.

After distillation of the unreacted monomer, and subse-
quent stripping under vacuum at 150°C for 3 hours, 180 mg of
the polymer are separated.

The IR analysis of the obtained polymer shows that, in
the spectrum, absorption bands in the zone of the fluorinated
double bonds are absent.

The ^{19}F-NMR analysis carried out on the polymer dissolved

in C_6F_6 is in accordance with the homopolymer structure having a molecular weight of 50,000. The analysis does not show the presence of unreacted monomer.

The DSC thermogram does not show any melting endothermic curve, wherefore the polymer is amorphous. The polymer T_g, determined by DSC, is -35.4°C. The thermogravimetric analysis (TGA) shows a weight loss of 2% at 332°C and of 10% at 383°C.

EXAMPLE 8

Copolymer between perfluoro-3,5,8-trioxa-1-nonene $CF_3OCF_2CF_2OCF_2OCF=CF_2$ (MOVE 2) and perfluoro-3,5,7-trioxa-6,methyl-1-octene $CF_3OCF(CF_3)OCF_2O-CF=CF_2$ (MOVE 2a).

In a reactor having the same characteristics as that described in Example 7, 150 μl of perfluoropropionylperoxide at 3% by weight in $CFCl_2CF_2Cl$ and 3.2 g of a mixture prepared according to the process of Example 5 and containing 83% MOVE 2 and 17% MOVE 2a, are introduced. The reactor is then evacuated, cooled, and the subsequent reaction carried out as described in the previous Example 7.

The reaction raw material appears as a slightly viscous, transparent, colourless and homogeneous solution. The monomers which have not reacted are distilled and a stripping under vacuum at 150°C for 3 hours is in sequence carried out. Finally 350 mg of the polymer are separated.

The IR analysis shows that, in the polymer spectrum, absorption bands in the zone of the fluorinated double bonds are absent.

The ^{19}F-NMR analysis is in accorddnce with the copolymer structure having an average molecular weight of 35,000 and a MOVE 2/MOVE 2a content equal to the percentages of the reacting mixture; unreacted monomers are not evident.

The DSC thermogram does not show any melting endothermic curve, wherefore the polymer is amorphous. The polymer T_g, determined by DSC, is -52.6°C. The thermogravimetric analysis (TGA) shows a weight loss of 2% at 280°C and of 10% at 327°C.

EXAMPLE 9

Crystalline copolymer between MOVE 1 and TFE.

    A 5 1 steel AISI 316 autoclave with stirrer working at 650 rpm has been used. After the vacuum has been effected, 3 1 of demineralized water, 15.70 g of MOVE 1 and the microemulsion prepared according to the procedure described in United State Patent 4,864,006 are in sequence introduced, so as to have a concentration of 2 g of surfactant/l of water.

    The autoclave is heated up to 75°C and then 0.32 bar of ethane are introduced. A gaseous mixture in a molar ratio of 54.55 TFE/MOVE 1 is pumped by a compressor until having inside the autoclave a pressure of 21 absolute bar.

    The composition of the gaseous mixture present in the autoclave top is analyzed by gas chromatography.

    Before the reaction starting the gaseous phase results to be formed by the following molar percentages of the reactants: 93.1% TFE, 5.5% MOVE 1 and 1.4% Ethane. The reaction is triggered by feeding in a continuous way by a metering pump a potassium persulphate 0.0031 molar solution at a flow rate of 88 ml/h.

    The pressure is maintained constant by feeding the monomer mixture. The polymer synthesis is stopped after 742 g of mixture have been fed in total.

    The reactor is cooled at room temperature, the emulsion is discharged and the coagulation is induced by HNO_3 (65%) addition.

    The polymer is separated, washed with water and dried at 220°C.

    The IR analysis shows the presence of very small absorption bands in the carboxyl zone, whose intensity results to be half of the one obtained from a TFE/PVE copolymer film having the same thickness, prepared according to the comparative Example 3. MFI according to ASTMD 1238-52T was 4.4. The polymer therefore results thermally more stable (see the comparative Example hereunder).

EXAMPLE 10

Amorphous copolymer between MOVE 1 and TFE.

In an AISI-316 polymerization reactor having a 40 ml volume, equipped with magnetic stirring, pressure transducer and an inlet for the reactant feeding and discharge, 250 μl of perfluoropropionylperoxide at 3% by weight in $CFCl_2CF_2Cl$, 9.8 mmoles of MOVE 1 and 18 mmoles of tetrafluoroethylene are introduced.

The reactor is cooled to the temperature of -196°C, evacuated, then brought to room temperature. The procedure and cooled as repeated twice.

At the end of the degassing operations the reactor is thermostated at the temperature of 30°C and the reaction mixture maintained under magnetic stirring. The internal pressure decreases from 6.4 atm to 4.7 atm in about 8 hours (reaction time).

After distillation of the unreacted monomers and polymer stripping under vacuum for 3 hours at 150°C, 1,100 mg of polymer are recovered. The polymer appears as a transparent and colourless rubber.

By ^{19}F-NMR analysis of the polymer dissolved under heating in C_6F_6 it is determined that the MOVE 1 molar percentage in the polymer is 24%.

The IR analysis does not show, in the polymer spectrum, absorption bands in the zone of the fluorinated double bonds, and shows the presence of very small absorption bands in the zone of the carboxyl signals. The intensity of these signals, compared with the similar ones obtained from a film having the same thickness obtained with the polymer of the comparative Example 1, is equal to about 1/10 of the latter.

The DSC thermogram does not show any melting endotherm, wherefore the polymer is amorphous. The T_g determined by DSC is -21.4°C.

The TGA shows a weight loss of 2% at 450°C and of 10% at 477°C. The polymer therefore results thermally more stable (see the comparative Example hereunder) with respect to the

comparative Example (see below).

The polymer intrinsic viscosity measured at 30°C in Fluorinert® FC-75, is 35.5 ml/g.

EXAMPLE 11

Amorphous copolymer between MOVE 1 and TFE.

In an AISI-316 polymerization reactor identical to that described in the previous Example 10, 250 μl of perfluoropropionylperoxide at 3% by weight in $CFCl_2CF_2Cl$, 9.75 mmoles of MOVE 1 and 9 mmoles of tetrafluoroethylene are introduced in sequence.

The procedure already described in the previous Example 10 is followed until the thermostating step at the temperature of 30°C under magnetic stirring. During the reaction the internal pressure decreases from 3.4 atm to 2.9 atm in about 8 hours.

At the end the unreacted monomers are distilled and the polymer is stripped under vacuum at 150°C for 3 hours.

480 mg of the polymer are separated.

By ^{19}F-NMR analysis of the polymer dissolved under heating in C_6F_6 it is determined that the MOVE 1 molar percentage in the polymer is 39%.

The IR analysis shows that, in the polymer spectrum, absorption bands in the zone of the fluorinated double bonds are absent.

The DSC thermogram does not show any melting endothermic curve, wherefore the polymer is amorphous. The T_g determined by DSC is -29.8°C.

The TGA shows a weight loss of 10% at 435°C.

EXAMPLE 12

Amorphous copolymer between MOVE 1 and $CF_2=CH_2$

In a polymerization reactor identical to that described in Example 10, 250 μl of perfluoropropionylperoxide at 3% by weight in $CFCl_2CF_2Cl$, 10 mmoles of MOVE 1, and 18 mmoles of VDF are introduced in sequence.

The procedure already described in the previous Example

10 is followed until the thermostating step at the temperature of 30°C under magnetic stirring. The internal pressure decreases from 6.8 atm to 5.0 atm during the reaction (about 8 hours).

After distillation of the unreacted monomers and subsequent polymer stripping under vacuum at 150°C for 3 hours, 1,600 mg of the polymer are separated, appearing as a transparent and colourless rubber.

By the ^{19}F-NMR analysis carried out on the polymer dissolved in C_6F_6, it is determined that the MOVE 1 molar percentage in the polymer is 40%.

The DSC termogram does not show any melting endothermic curve, wherefore the polymer is amorphous. The T_g determined by DSC, is -47°C.

The TGA shows a weight loss of 2% at 428°C and of 10% at 455°C.

EXAMPLE 13

Amorphous terpolymer MOVE 2/MOVE 2a/TFE.

In a polymerization reactor identical to that described in Example 10, 100 μl of perfluoropropionylperoxide at 6% by weight in $CFCl_2CF_2Cl$, 10 mmoles of a MOVE 2 (83%) and MOVE 2a (17%) mixture synthetized according to the process of Example 5, and 18 mmoles of tetrafluoroethylene (TFE) are in sequentially introduced.

The procedure already described in the previous Example 10 is then followed until thermostating at the temperature of 30°C under magnetic stirring. The internal pressure decreases from 6.1 atm to 3.9 atm during the reaction (about 8 hours).

After distillation of the unreacted monomers and polymer stripping under vacuum at 150°C for 3 hours, 1,131 mg of the polymer are separated.

By the ^{19}F-NMR analysis carried out on the polymer dissolved in C_6F_6 it results that the total molar percentage of the MOVE 2 + MOVE 2a perfluorovinyl ethers units in the polymer is 22%; the MOVE 2/MOVE 2a ratio by moles in the

polymer is 83/17 and it is equal to that of the starting feed mixture.

The presence of unreacted monomers is not evident.

The IR analysis does not show, in the polymer spectrum, absorption bands in the zone of the fluorinated double bonds, and it shows the presence of very small absorption bands in the zone of the carboxyl signals. The intensity of these signals, compared with the similar ones obtained from a film having the same thickness obtained with the polymer of the comparative Example 1, is equal to about 1/10 of the latter.

The DSC thermogram does not show any melting endotherm, wherefore the polymer is amorphous. The T_g determined by DSC, is -37.5°C.

The TGA shows a weight loss of 10% at 473°C.

The polymer intrinsic viscosity measured at 30°C in Fluorinert® FC-75, is 40.0 ml/g.

EXAMPLE 14

Amorphous terpolymer MOVE 2/MOVE 2a/TFE.

In a polymerization reactor identical to that described in Example 10, 100 μl of perfluoropropionylperoxide at 6% by weight in $CFCl_2CF_2Cl$, 9.7 mmoles of the MOVE 2 (83%) and MOVE 2a (17%) mixture synthesized according to the process of Example 5, and 10 mmoles of tetrafluoroethylene (TFE) are in sequence introduced.

The procedure already described in the previous Example 10 is then followed until the thermostating step at the temperature of 30°C under magnetic stirring. The internal pressure decreases from 3.6 atm to 2.7 atm during the course of reaction (about 8 hours).

After distillation of the unreacted monomers and polymer stripping under vacuum at 150°C for 3 hours, 652 mg of polymer are separated.

By the ^{19}F-NMR analysis carried out on the polymer dissolved in C_6F_6 it results that the total molar percentage of units derived from the MOVE 2 + MOVE 2a perfluorovinyl ethers

in the polymer is 37%; the MOVE 2/MOVE 2a molar ratio in the polymer is 83/17 and it is equal to that of the starting feed mixture.

The presence of unreacted monomers is not evident.

The IR analysis does not show, in the polymer spectrum, absorption bands in the zone of the fluorinated double bonds.

The DSC thermogram does not show any melting endothermic curve, wherefore the polymer is amorphous. The T_g determined by DSC, is -44.5°C.

The TGA shows a weight loss of 10% at 451°C.

The polymer intrinsic viscosity measured at 30°C in Fluorinert® FC-75, is 16.7 ml/g.

EXAMPLE 15

Amorphous copolymer between perfluoro-1,2-dihydro-3,5,8-trioxa-1-nonene (H-MOVE 2) and perfluoro-1,2-dihydro-3,5,7-trioxa-6-methyl-1-octene (H-MOVE 2a) with molar ratio 88/12.

In a reactor identical to that described in Example 7, 200 μl of perfluoropropionylperoxide at 3% by weight in CFCl$_2$-CF$_2$Cl and 3.1 g of an 88/12 H-MOVE 2/H-MOVE 2a 88/12 mixture are introduced.

The procedure described in Example 7 is followed.

The recovered reaction raw material appears as a slightly viscous, transparent, colourless and homogeneous solution.

After distillation of the unreacted monomer and subsequent stripping under vacuum at 150°C for 3 hours, 120 mg of polymer are separated.

The IR analysis of the obtained polymer shows that, in the polymer spectrum, absorption bands in the zone of the fluorinated double bonds are absent.

The ^{19}F-NMR analysis is in accordance with the copolymer structure having a content of monomers H-MOVE 2 and H-MOVE 2a equal to the H-MOVE 2 and H-MOVE 2a percentages in the reacting mixture. The analysis does not show the presence of

unreacted monomers.

The DSC thermogram does not show any melting endotherm, wherefore the polymer is amorphous. The polymer T_g determined by DSC, is -58.0°C. The thermogravimetric analysis (TGA) shows a weight loss of 10% at 307°C.

EXAMPLE 16

Terpolymer H-MOVE 2/H-MOVE 2a/TFE.

In a reactor similar to that described in Example 10, 100 μl of perfluoropropionylperoxide at 6% by weight in $CFCl_2$-CF_2Cl and 5 mmoles of a H-MOVE 2 (88%) and H-MOVE 2a (12%) mixture and 18 mmoles of tetrafluoroethylene, are introduced.

The same procedure described in Example 10 is followed.

At the end of the degassing, the reactor is thermostated at the temperature of 30°C under magnetic stirring. The internal pressure decreases from 6.8 atm to 6.5 atm in about 6 hours (reaction time).

After distillation of the unreacted monomers and polymer stripping under vacuum at 150°C for 3 hours, 300 mg of the polymer are separated.

By ^{19}F-NMR analysis of the polymer dissolved under heating in C_6F_6 it is calculated that the molar percentage (mole %) of units derived from the perfluorovinyl ethers (H-MOVE 2 + H-MOVE 2a) contained in the polymer is 33%. The H-MOVE 2/H-MOVE 2a molar ratio in the polymer is equal to the H-MOVE 2/H-MOVE 2a molar ratio of the feed mixture. Unreacted monomers are not evident.

The IR analysis does not show, in the polymer spectrum, absorption bands in the zone of the fluorinated double bonds.

The DSC thermogram does not show any melting endotherm, wherefore the polymer is amorphous. The T_g determined by DSC, is -44.5°C.

The TGA shows a weight loss of 10% at 450°C.

EXAMPLE 1 (comparative)

Copolymer PVE/TFE.

In a polymerization reactor identical to that described

in Example 10, 250 μl of perfluoropropionylperoxide at 3% by weight in CFCl$_2$CF$_2$Cl, 9.8 mmoles of PVE and 18 mmoles of tetra-fluoroethylene, are in sequence introduced.

The procedure already described in the previous Example 10 is followed until thermostating at the temperature of 30°C under magnetic stirring. The reaction time is eight hours.

After distillation of the unreacted monomers and stripping under vacuum at 150°C for 3 hours, 540 mg of the polymer are recovered.

By the ^{19}F-NMR analysis carried out on the polymer dissolved in C$_6$F$_6$ it is calculated that the PVE molar percentage in the polymer is 23%.

The IR analysis shows that, in the polymer spectrum, there are absorption bands in the carboxyl zone, whose intensity is 10 times higher than that obtained from a MOVE 1/TFE copolymer film prepared according to Example 10, and having the same thickness.

The DSC thermogram does not show any melting endothermic curve, wherefore the polymer is amorphous. The TGA shows a weight loss of 2% at 427°C and of 10% at 463°C. The Tg, determined by DSC, is + 15°C.

The polymer intrinsic viscosity, measured at 300C in Fluorinert® FC-75, is 51 ml/g.

EXAMPLE 2 (comparative)

Copolymer between β-PDE (CF$_3$OCF$_2$CF$_2$OCF=CF$_2$)/TFE.

In a polymerization reactor identical to that described in Example 10, 250 μl of perfluoropropionylperoxide at 3% by weight in CFCl$_2$-CF$_2$Cl, 10 mmoles of β-PDE, and 18 mmoles of te-trafluoroethylene, are in sequence introduced.

The procedure described in the previous Example 10 is followed until the thermostating step at the temperature of 30°C under magnetic stirring.

By the ^{19}F-NMR analysis carried out on the polymer purified of monomers by the processes described in the previous

Examples, it is calculated that the molar percentage of β-PDE in the polymer is 23%.

The DSC thermogram does not show any melting endothermic curve wherefore the polymer is amorphous. The T_g, determined by DSC, is -4.8°C.

This Tg value is clearly higher than those obtainable with the vinyl ethers of the invention (see the above Examples).

EXAMPLE 3 (comparative)

Crystalline copolymer PVE/TFE (PFA).

One operates as in Example 9 except that in this case the perfluoropropylvinyl ether (PVE) is used instead of α-PDE to obtain a copolymer having MFI equal to that of the Example copolymer of9.

The IR analysis shows absorption bands in the carboxyl zone, the intensity is of which double those obtained for a TFE/MOVE 1 copolymer film of equal thickness and prepared according to Example 9.